Detection of wine adulteration using NIR spectroscopy and diffuse reflectance

MATE MAGYAR AGRÁR- ÉS ÉLETTUDOMÁNYI EGYETEM

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Abstract

Food adulteration is in the focus of research due to its negative effect on safety, nutritional value and because of the demand of protection of brand, regional origin. Wine is one of the most sensitive food products since the quality primarily depends on the plant cultivar, the geographic origin and the production year, as well. Addition of water and sugar is not allowed at all for wine products. Presented study investigated the feasibility of non-destructive methods to detect such adulteration. Wines of Portugieser (2009, Szekszárd, Hungary) and Sauvignon Blanc (2009, Etyek-Buda, Hungary) were selected for experiments. The instrument of DLP® NIRscan™ Nano (Texas Instrument) was used to collect near infrared spectra in the range of 900-1700 nm. Spectra were preprocessed using standard normal variate (SNV). Partial least squares regression (PLSR) was performed on NIR spectra to predict adulteration level, if any. Low power laser modules (3 mW) were used to collect diffuse reflectance signals at wavelengths of 532, 635, 780, 808, 850, 1064 nm. Digital images were collected using a 12 bit camera (Photonfocus MV1-D1312) with 0.113 mm/pixel resolution. Intensity signal collected around the incident point of the laser beam was processed and compared to detect changes. The presented preliminary study obtained promising results. Introduced techniques might be suitable for rapid non-destructive detection of wine adulteration. Findings must be confirmed with large sample set and wide range of products before industrial deployment.

	Red wine			White wine		
	Sugar	Water	Mixed	Sugar	Water	Mixed
LV	3	3	6	3	3	6
R2	0.9990	0.9997	0.9891	0.9992	0.9998	0.9913
RMSE	0.166%	0.504%	0.194	0.165%	0.361%	0.180

Table 1: Adulteration detection results by PLSR model

According to the summary report in Table 1, mixed samples reached high accuracy using 6 LV meanwhile single ingredient change was detected already with 3 LV. This applies to both red and white wines. Prediction error (RMSE) is reported in % for sugar and water, while adulteration level is used for mixed samples. Adulteration level is the distance of measured sample from original wine. All determination coefficients show very good fit with $R^2 > 0.989$.

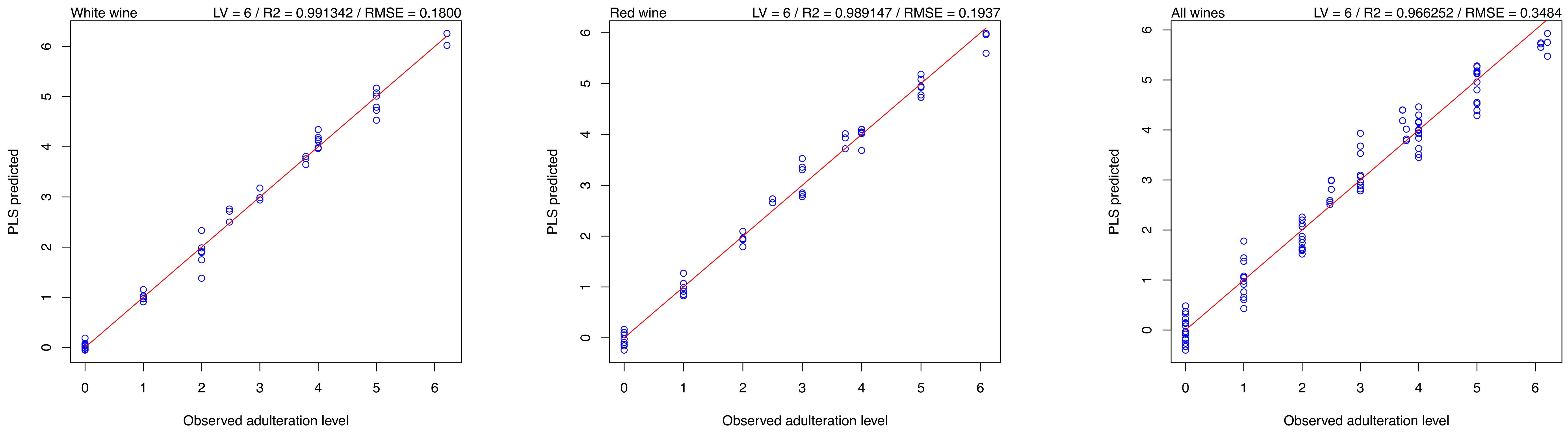

Figure 1: PLSR results for wine adulteration with additional sugar and water dilution (0 level denotes original sample)

Materials and methods

Materials

Bottled wine samples, produced in Hungary, were used in the experiment. Two wines were selected to represent both white and red types, a Portugieser (2009, Szekszárd, Hungary) and a Sauvignon Blanc (2009, Etyek-Buda, Hungary). Adulteration was performed using water and sugar. Additional materials were applied in 5 steps, making a dilution sequence on the basis of 100 ml. Addition of sugar resulted in different concentration for red and white wines due to the variable weight of sugar cubes (approximately 3.7 g, "Koronás cukor" produced by Magyar Cukor Zrt, Hungary). Mixed samples were also made to test whether combined adulteration can be detected. Each sample was measured with three replicates.

Near Infrared Spectroscopy

The Near Infrared (NIR) spectra of samples were collected using DLP® NIRscan™ Nano (Texas Instrument) device. Spectral readings were acquired in the wavelength range of 900 – 1700 nm. Temperature was adjusted to 25 ± 0.1 °C during the measurement. Data were subjected to Standard Normal Variate (SNV) preprocessing to avoid offset effect in comparisons.

Laser induced diffuse reflectance imaging

Wine samples were poured into Petri dish in 3 mm level. Low power laser modules of 3 mW were used to induce diffuse reflectance (backscattering) signals at wavelengths of 532, 635, 780, 808, 850 and 1064 nm. Digital images were collected using a 12 bit camera (Photonfocus MV1-D1312) with 0.113 mm/pixel resolution. Image acquisition took place in a darkroom to enhance signal and protect measurement from other light sources. Binary data was processed using GNU Octave (version 4.4.1) software.

Data Analysis

The statistical software of R (version 4.0.3, R Foundation for Statistical Computing, Vienna, Austria) was used to fit models and evaluate results.

Sugar								
Wavelength	D75	D50	D25	R5075	R2575	A50	A2575	RA
1064 nm	*	*	*			**	*	+
850 nm	*		*			*	*	+
808 nm			*				+	
780 nm			*	+			*	
635 nm	+		*	*		+	*	
532 nm							*	**

Table 2: ANOVA results for laser backscattering on addition of sugar
Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 '

Water								
Wavelength	D75	D50	D25	R5075	R2575	A50	A2575	RA
1064 nm								
850 nm								
808 nm	+			+			+	
780 nm							+	
635 nm				+	*			
532 nm					*		*	***

Table 3: ANOVA results for laser backscattering on addition of water
Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 '

According to ANOVA results (Table 2-3), adulteration with sugar induced response of parameters D25 and A2575. The wavelength 1064 nm was the most sensitive to changes in sugar content. In case of water dilution, paremeters R2575 and A2575, wavelength 532 nm shown similar sensitivity.

Conclusions

The relationship between adulteration and NIR spectra was explored for both red and white wine samples. PLSR model was successful in detection of adulteration. The common model was less accurate than that of single wine type. Diffuse reflectance responded sensitively to changes but was not able to build good prediction model yet.